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Use of Bi-2223 Superconducting Tapes Sheathed with Ag-Au Alloys for a Passive Thermoelement

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The possibility of applying the newly developed Bi-2223 superconducting tape sheathed with Ag-Au alloy to the thermoelectric refrigerator device was investigated. The tape sheathed with Ag-Au alloy has the transition temperature (T_c) 108K and the thermal conductivity as low as 0.2W/cmK at 77K. The tape is also flexible and shows the very low contact resistance. Thus the tape satisfies desirable conditions as a passive thermoelement for the use near the liquid nitrogen temperature. The figure of merit of the two leg thermocouple which consists of the n-type Bi-Te single crystal and the thinner Ag-Au sheathed Bi-2223 tape was theoretically estimated to be superior to that of the n-type Bi-Te/Bi-2223(polycrystal) thermocouple below Tc.

I. INTRODUCTION

A target of thermoelectric refrigeration is to realize a solid state refrigerator at low temperatures. Various experiments at low temperatures is indispensable to understand the intrinsic properties of physical and chemical phenomena. Low temperature experiments between 77K and 300K can be easily performed using liquid nitrogen at low cost. However, lower temperature experiments below 77K can not be performed easily, because more expensive apparatus or coolant must be used such as liquid helium or a Gifford-McMahon (G-M) helium refrigerator. If the thermoelectric element efficient at low temperatures can realize the inexpensive and silent automated refrigerator, it is useful for various experiments such as the optical experiments which are apt to be easily damaged by vibration.

The thermoelectric properties of the thermoelectric semiconductor drastically deteriorare at low temperature because of a decrease in the contents of charge carriers. Though the property of n-type $Bi_{1-x}Sb_x$ alloy is recognized to be the best material at low temperature, that of the p-type $Bi_{1-x}Sb_x$ is extremely inferior to the n-type one, and it is of no practical use [1].

Since the discovery of high temperature oxide superconductors with the transition temperature (T_c) higher than the boiling point of liquid nitrogen, several proposals have been made to use the oxide superconductor as the passive thermoelement of the thermocouple in place of a low-efficient p-type thermoelectric semiconductor [2]. The figure of merit of the superconductor is theoretically infinite because the electrical resistivity is zero when the element is used at a temperature below T_c. Therefore, the figure of merit will be improved below T_c. In the past, sintered superconducting polycrystals such as Bi-2223 (T_c=110K) and YBCO (T_c=90K) have been investigated as a passive thermoelement [3]. However, there were much problems such as large contact resistance and small critical current density (J_c). The use of the superconducting tape sheathed with pure Ag is a solution to the problem. Though these tapes can be easily soldered and attain the high J_c [4], the high thermal conductivity of the pure Ag sheath, however, causes a serious problem of the heat intrusion.

A use of Ag-Au alloy as a metal stabilizer in stead of pure Ag has been proposed by Hitachi Cable Ltd., and the reactivity with Bi-based oxide superconductors was investigated [5]. We also measured the thermal and electrical properties of the alloy tapes [6]. As the results, it was found that the alloys did not react with the superconductors and that the thermal and electrical conductivity of the Ag-Au alloy tapes drastically decreased with increasing Au content. Bi-2223 superconducting tapes sheathed with Ag-Au alloy showed the low thermal conductivity.

In this paper, we theoretically and experimentally investigated the possibility of applying the Bi-2223 [$(BiPb)_2Sr_2Ca_2Cu_3O_x$] superconducting tape sheathed with Ag-Au alloy to a passive thermoelement. The characteristics were also compared with those of the sintered Bi-2223 polycrystal.

II. EXPERIMENTAL

Ag-Au alloy tapes and Bi-2223 superconducting tapes sheathed with the alloy were fabricated by Hitachi Cable Ltd. The tape was about 120μm in thickness and about 3mm in width. The superconductor cross section ratio f_{sc} is defined by the ratio of the cross section of the core superconductor to the total cross section of the tape. Sintered Bi-2223 superconducting polycrystal was fabricated by a conventional solid state reaction method to evaluate the thermal conductivity of the core superconductor.

Thermoelectric n-type Bi-Te system single crystals were fabricated using a vertical Bridgman method in a vacuum sealed ampoule. The crystal was cut in the size of 3mm x 3mm x 10mm. The n-type

Bi-Te and the superconducting tape were joined at their ends by soldering, and the thermoelectric element (thermocouple) was constructed.

The refrigeration property of the passive thermoelement was measured by a cryostat using liquid nitrogen from 77K to 300K. The f_{SC} value was decided from observations of the tape cross section using an optical microscope.

III. CALCULATION

In the passive thermoelement, if the length of the two legs is equal, the figure of merit is defined by

$$Z=\frac{(\alpha_{SC}+|\alpha_n|)^2}{\rho_{SC}(\kappa_{SC}+\kappa_n\frac{A_n}{A_{SC}})+\rho_n(\kappa_n+\kappa_{SC}\frac{A_{SC}}{A_n})} \quad (1),$$

where α_n, ρ_n, κ_n and A_n are a Seebeck coefficient, an electrical resistivity, a thermal conductivity and a cross section of the n-type Bi-Te material, respectively, and α_{SC}, ρ_{SC}, κ_{SC} and A_{SC} are those of the Bi-2223 superconducting tape sheathed with Ag-Au alloy, respectively [7]. The cross section ratio m_{SC} is defined by the cross section ratio of the superconducting tape to the n-type Bi-Te, A_{SC}/A_n. In this calculation, we defined A_n constant at 3 x 3 mm^2. In the superconducting state, in which α_{SC} and ρ_{SC} is zero, Z can be rewritten as Eq.(2);

$$Z=\frac{\alpha_n^2}{\rho_n(\kappa_n+\kappa_{SC}m_{SC})} \quad (2)$$

We calculated the temperature dependence of the figure of merit for the passive thermoelements using the measured parameters in the case of the various configurations of superconducting tapes such as f_{SC}, m_{SC} and Au content in the alloy sheath.

IV. RESULTS and DISCUSSION

4.1 Thermal and electrical properties of Ag-Au alloy tapes

Firstly, we summarize our previous works of thermal and electrical conductivity of Ag-Au alloy tapes [6]. Figure 1 shows the temperature dependence of the thermal conductivity of the heat treated Ag-Au alloy tapes (κ_{alloy}) with various contents of Au up to 30at.%. κ_{alloy} drastically decreased with increasing Au content at low temperatures. For example, the thermal conductivity of the tape with 15at.%Au was by about three orders smaller than that of the pure Ag tape at 20K. Figure 2 shows the temperature dependence of the electrical resistivity of the heat treated Ag-Au alloy tapes. The electrical resistivity drastically increased with an increase in the Au content at low temperatures. For example, the electrical resistivity of the Ag+15at.%Au alloy tape was by about three orders larger than that of the pure Ag tape at 20K. Since the electronic thermal conductivity and the electrical resistivity are related to one another by the Wiedemann-Franz law, the Au content dependences in Figs.1 and 2 may be reasonable. Thus, the thermal and electrical conductivity of the Ag-Au alloy tape was confirmed to decrease drastically with an increase of the Au content.

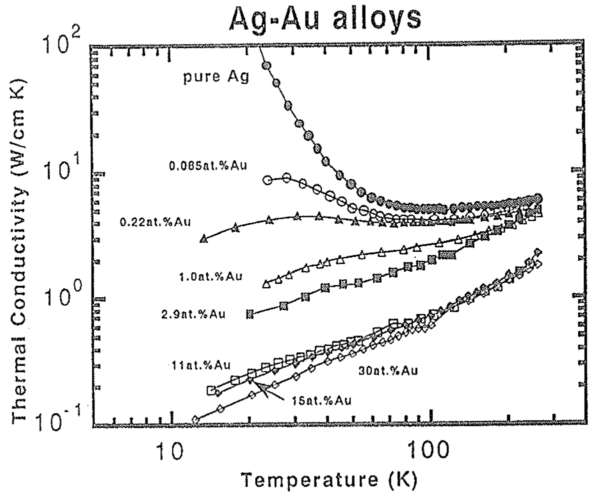

Fig.1 Temperature dependence of the thermal conductivity of Ag-Au alloy tapes with the various concentrations of Au.

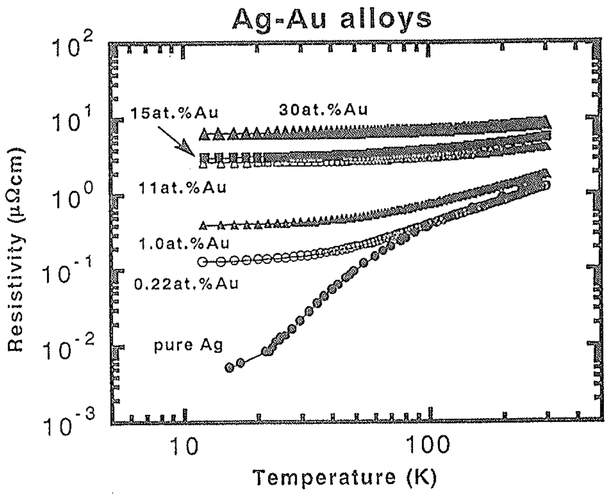

Fig.2 Temperature dependence of the electrical conductivity of Ag-Au alloy tapes with the various concentrations of Au.

4.2 Characteristics of Bi-2223 superconducting tapes sheathed with Ag-Au alloy

Figure 3 shows the temperature dependence of the electrical resistivity of the Bi-2223 superconducting tape (f_{SC}=0.33) sheathed with Ag+15at.%Au alloy. Electrical resistivity of a sintered Bi-2223 polycrystal

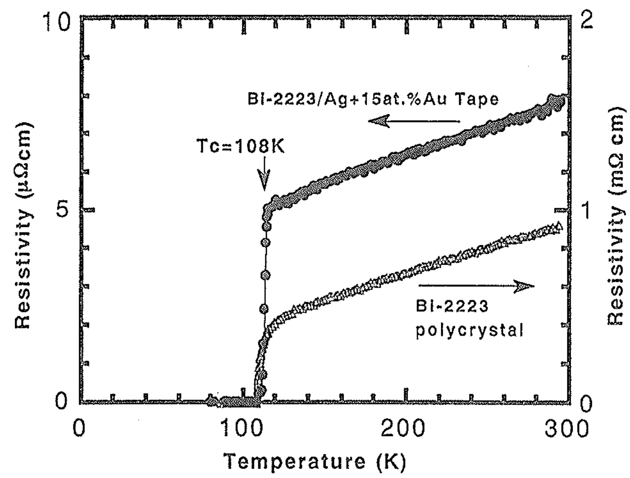

Fig.3 Temperature dependence of the electrical resistivity of Bi-2223 superconducting tape sheathed with Ag+15at.%Au alloy and Bi-2223 sintered polycrystal. Tc was about 108K.

is also shown in the same figure for comparison. Transition temperature T_C of the tape was about 108K. In the normal state, the electrical resistivity of the tape is by about three orders smaller than that of the sintered polycrystal.

Figure 4 shows the thermal conductivity of the Bi-2223 superconducting tape sheathed with Ag+15at.%Au alloy (f_{SC}=0.33), κ_{AgAuT}, as compared with those of the Bi-2223 tape (f_{SC}=0.23) sheathed with pure Ag, κ_{AgT}, the sintered Bi-2223 sintered polycrystal κ_{poly} and a Cu-Zn alloy. κ_{AgAuT} was about 0.2W/cmK at 77K which was comparable to that of the Cu-Zn alloy [8].

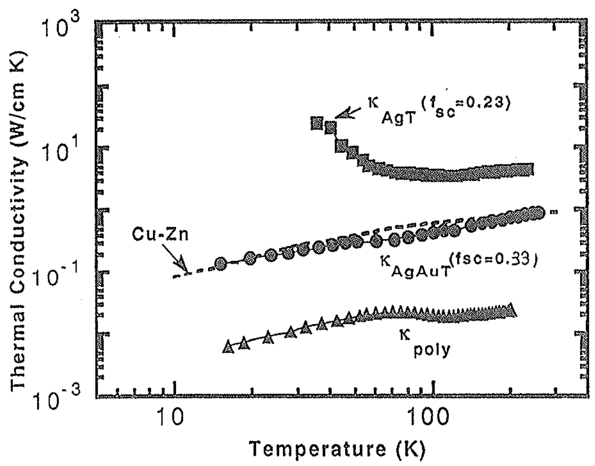

Fig.4 Temperature dependence of thermal conductivities of both the Bi-2223 superconducting tapes sheathed with Ag+15at.%Au alloy (f_{SC}=0.33), κ_{AgAuT}, and with pure Ag (f_{SC}=0.23), κ_{AgT}. For comparison, thermal conductivities of the sintered Bi-2223 polycrystal κ_{poly} and a Cu-Zn alloy are also shown.

4.3 Characteristics of n-type Bi-Te single crystal

Figure 5 shows the temperature dependences of the thermal conductivity, the electrical resistivity and Seebeck coefficient for the n-type Bi-Te single crystal which was used in our investigations. The measured thermal conductivity was consistent with the reported value [9]. Since the growth conditions such as the doping level and the composition was not optimized, Seebeck coefficient was about 180μV/K at 300K which was smaller than that of the reported value [10].

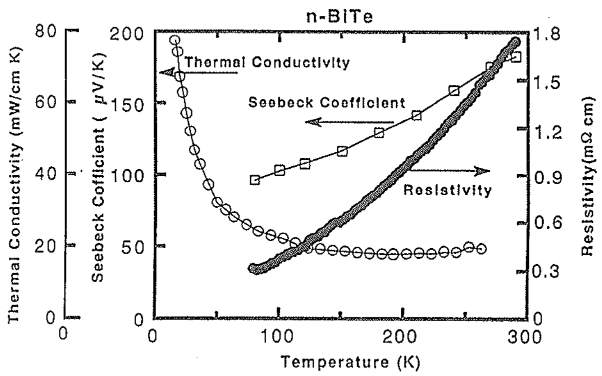

Fig.5 Temperature dependences of the thermal conductivity, the electrical resistivity and Seebeck coefficient for the n-type Bi-Te single crystal used in our investigations.

4.4 Calculation results of figure of merit for passive thermoelements

The figure of merit for the passive thermoelements, in which the superconducting tape was used, was calculated for the various structural parameters of the tape. The figure of merit of superconducting tape changes with a change in the Au content in the alloy sheath, the superconductor cross section ratio in the tape, f_{SC} and the cross section ratio, m_{SC}, respectively. The calculation was performed within the conditions which were possible to realize.

Figure 6 shows the relation between the figure of merit of the thermoelement and the operating temperature as a function of m_{SC}. The Bi-2223 superconducting tape (f_{SC}=0.4) sheathed with Ag+15at.%Au alloy was used as a superconducting leg. The figure of merit increases by decreasing the ratio m_{SC} below T_C, and approaches to the constant value of the n-type Bi-Te. The m_{SC} value of 0.067, which corresponds to the size of the superconducting tape of 20μm in thickness and 3mm in width, can be realized. In order to maximize the figure of merit below T_C, m_{SC} should be as low as possible.

Figure 7 shows the relation between the figure of merit of the thermoelement and the operating temperature as a function of f_{SC}. Bi-2223 tape (m_{SC}=

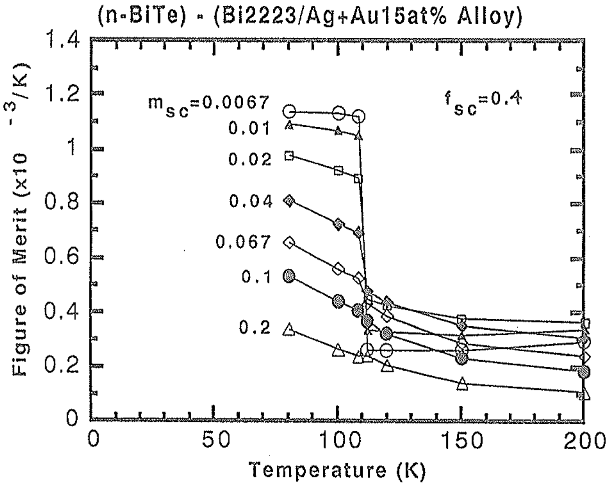

Fig.6 Theoretical relation between the figure of merit of the thermoelement and the operating temperature as a function of m_{SC}. Bi-2223 superconducting tape (f_{SC}=0.4) sheathed with Ag+15at.%Au alloy was used as a superconducting leg.

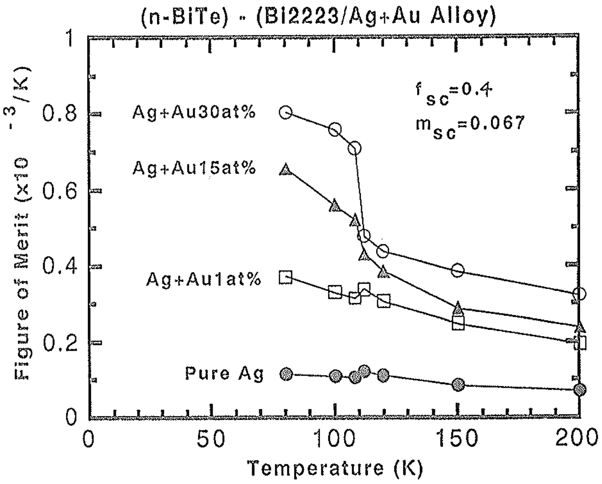

Fig.8 Theoretical relation between the figure of merit of the thermoelement and the Au content in the alloy sheath of the Bi-2223 tape. The f_{SC} value of the tape and m_{SC} are kept constant at 0.4 and 0.067, respectively.

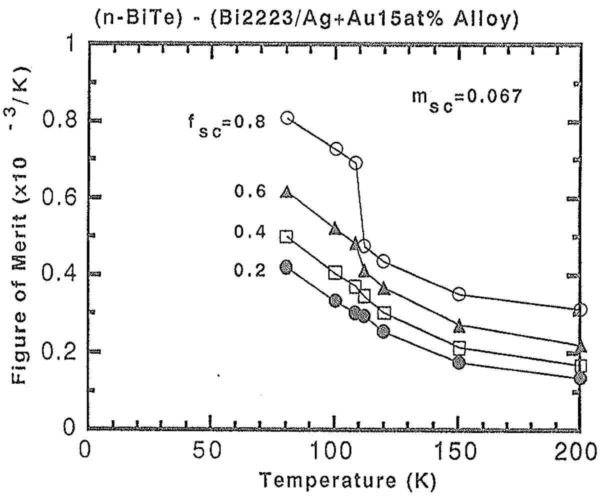

Fig.7 Theoretical relation between the figure of merit of the thermoelement and the operating temperature as a function of f_{SC}. Bi-2223 tape (m_{SC}=0.067) sheathed with Ag+15at.%Au alloy was used as a superconducting leg.

0.067) sheathed with Ag+15at.%Au alloy was used as a superconducting leg. The figure of merit increases by increasing the f_{SC} value, especially below T_C, because the thermal conductivity of the superconducting core is smaller than that of the sheathing alloy. It is necessary to increase the f_{SC} value to increase the figure of merit.

Figure 8 shows relation between the figure of merit of the thermoelement and the Au content in the alloy sheath. The f_{SC} value of the Bi-2223 tape and m_{SC} were kept constant at 0.4 and 0.067, respectively. The figure of merit increased with increasing the Au content in the alloy sheath because of a decrease in the thermal conductivity.

For comparison, the calculation was performed also in the case that the sintered Bi-2223 polycrystal was used in the superconducting leg of the passive thermoelement. Figure 9 shows the temperature dependence of the figure of merit as a function of the m_{SC} value. In the case using the sintered Bi-2223 polycrystal, because of difficulty to cut the smaller superconducting chip, the m_{SC} value smaller than about 0.2 can not be realized in the actual fabrication. Though the figure of merit using the sintered Bi-2223 polycrystal has almost the same characters as that using the Bi-2223 tapes, the J_C value is smaller than that of the superconducting tape. When the integrated passive thermoelectric module is fabricated, the Bi-2223 superconducting tape sheathed with Ag-Au alloy may be a favorable material as a superconducting leg.

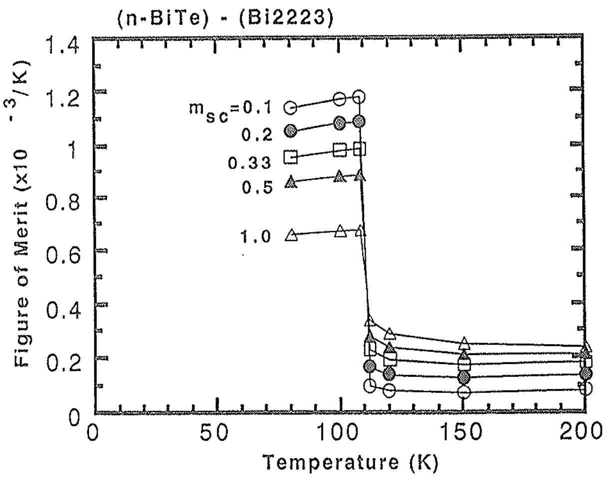

Fig.9 Temperature dependence of the figure of merit in the case of using the sintered Bi-2223 polycrystal for the superconducting leg, as a function of the m_{SC} value.

4.5 Experimental results of passive thermoelectric refrigeration

In order to confirm the results of the calculations, the refrigeration properties for the passive thermoelements were experimentally investigated. Figure 10 show the relation between the electric current applied to the element and the temperature difference ΔT as a function of the temperature of the hot junction. Bi-2223 superconducting tape sheathed with Ag+15at.%Au alloy (f_{SC}=0.4, m_{SC}=0.063) was used as a superconducting leg. The temperature difference was defined by $\Delta T=T_0-T_{cool}$, where T_0 and T_{cool} were the temperature of the cold junction before and after applying the electric current to the thermoelement, respectively. ΔT vs. the electric current curve has a maximum which is defined by ΔT_{max}. ΔT_{max} decreased with decreasing temperatures of the hot junction because of the decrease in the figure of merit of n-type Bi-Te mainly. In relation to the calculation results, how ΔT_{max} changes below T_C is very interesting but the increase in ΔT_{max} at 100K and 90K was not larger than that above T_C. Detailed investigation of this point remained to be a important theme for further research.

Figure 11 shows the relation between ΔT_{max} and the hot junction temperature of the thermoelement in which a various superconducting legs are used. ΔT_{max} increases in the case using the Bi-2223 tapes rather than using the Bi-2223 polycrystal which was cut as small a cross section as possible in our manipulation (m_{SC}=0.11). ΔT_{max} in the case of f_{SC}=0.4 is larger than f_{SC}=0.33, because of the lower thermal conductivity.

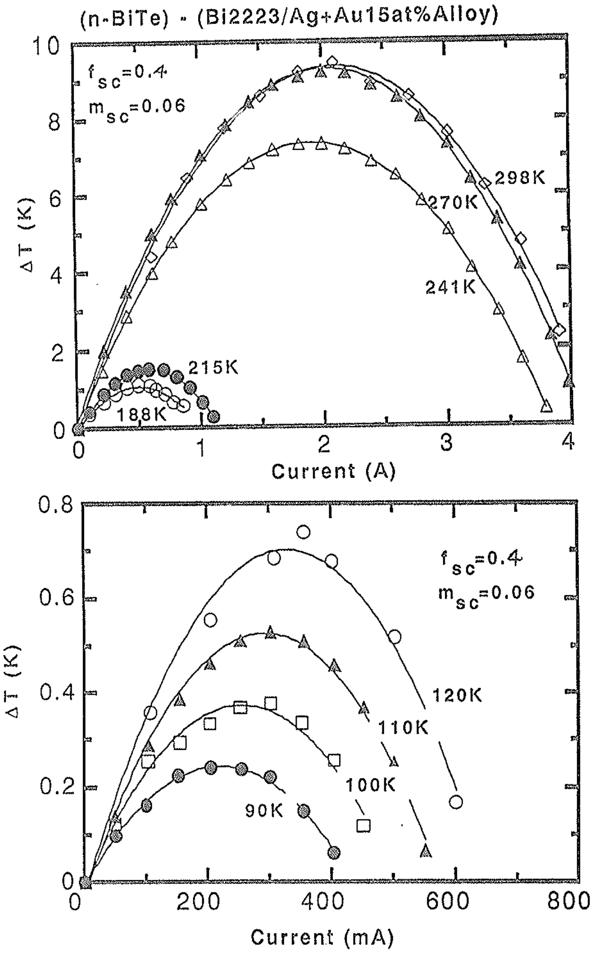

Fig.10 Experimentally obtained relation between the electric current applied to the thermoelement and the temperature difference ΔT as a function of the temperature of the hot junction. Bi-2223 superconducting tape sheathed with Ag+15at.%Au alloy (f_{SC}=0.4, m_{SC}=0.064) was used as a superconducting leg.

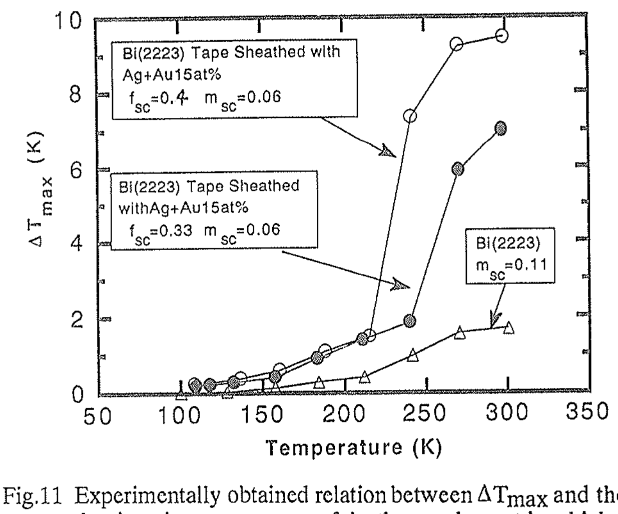

Fig.11 Experimentally obtained relation between ΔT_{max} and the hot junction temperature of the thermoelement in which a various superconducting legs are used.

V. SUMMARY

The possibility of applying the newly developed Bi-2223 superconducting tape to the thermoelectric refrigeration device at low temperatures was investigated. The tape sheathed with Ag+15at.%Au has the thermal conductivity as low as 0.2W/cmK at 77K. The theoretical estimation suggested that the figure of merit of the passive thermoelement which consists of the n-type Bi-Te single crystal and the Bi-2223 tape was superior. Thus the Ag-Au alloy sheathed tape satisfies desirable conditions as a passive thermoelement.

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